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Long-term geochemical evaluation of the coastal Chicot aquifer system, Louisiana, USA

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SUMMARY

Groundwater is increasingly being overdrafted in the Gulf and Atlantic Coastal regions of the United States. Geochemical data associated with groundwater in these aquifers can provide important information on changes in salinity, recharge, and reaction pathways that can be used to improve water management strategies. Here we evaluated long-term geochemical changes associated with the 23,000 km^2 Chicot aquifer system in Louisiana, USA. The Chicot aquifer is currently being overdrafted by about 1,320,000 m^3 per day. We compiled selected bulk geochemical data from samples collected from 20 wells in the Chicot aquifer from 1993 to 2015. Oxygen and hydrogen isotope measurements were additionally completed for the 2014 samples. We identified three zones of groundwater with distinctive geochemical character; (1) A groundwater recharge zone in the northern part of the study area with low pH, low salinity, and low temperature relative to other groundwater samples, (2) a groundwater recharge zone in the southeastern part of the study area with low temperature, high alkalinity, and higher Ca and Mg concentrations compared to the other groundwater samples, and (3) groundwater in the southwestern part of the aquifer system with high salinity, high temperature, and a ~1:1 Na/Cl ratio. The geochemistry of these regions has been relatively stable over the last ~20 years. However, in the drought year of 2011, the estimated extent of zones with elevated salinity increased substantially. Geochemical evidence suggests that there was increased infiltration of deeper, more salt-rich waters into the shallower Chicot aquifer.

1. Introduction

Groundwater is increasingly being overdrafted in the Gulf and Atlantic Coastal regions of the U.S., including states such as Louisiana, Alabama, Georgia, Florida, and South Carolina (e.g., Konikow, 2013; Liu et al., 2008; Hook et al., 2000). A recent investigation of decadal trends in water budget changes using satellite data from the Gravity Recovery and Climate Experiment (GRACE) highlights severe groundwater depletion in these coastal aquifer systems (Famiglietti and Rodell, 2013). In some areas the overuse of groundwater has led to increased saltwater intrusion near the coast and diminished base flow in streams further landward (e.g., Garza and Krause, 1996; Heywood and Griffith, 2013). Collection of water geochemical data is essential in these regions because it can be used for tracking salt water intrusion, delineating changes in recharge zones, identifying areas of groundwater surface water interaction, and identifying water–rock interaction pathways. The difficulty in applying this tool, however, is that the water chemistry of most aquifer systems in the region has not been effectively monitored over decadal or longer time periods. One exception is the Chicot aquifer system in Southwest Louisiana. Chemical data have been collected regularly from approximately 20 wells in the Chicot aquifer for well over a decade. The Chicot is the most used aquifer in the state of Louisiana and is being overdrafted by an estimated 1,320,000 m^3 per day (350 million gallons per day; Sargent, 2011).

In this study, we compile available bulk geochemical data, including pH, temperature (T), salinity, sodium (Na), calcium (Ca), magnesium (Mg), chloride (Cl), and alkalinity, to evaluate changes in the Chicot aquifer that have occurred from 1993 to 2015. These data are combined with new oxygen (O) and hydrogen (H) isotope measurements to identify zones of saltwater intrusion, recharge, and water–rock interaction. This geochemical evaluation provides insights into how the Chicot aquifer may evolve in response to continued (and possibly accelerated) pressures from drought and the demand for groundwater.

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2. Chicot aquifer

The Chicot aquifer, covering an area of 23,000 km^2, is the most-used source of fresh groundwater in Louisiana, accounting for 41% of all groundwater withdrawals (Sargent, 2011; Fig. 1). The Chicot is comprised of a series of unconsolidated sands, gravels, silts and clays of Holocene through Pliocene-age that were generated by the ancestral Mississippi River to the east and the smaller Sabine and Calcasieu Rivers to the west (Prakken, 2003; Tollett et al., 2003; Lovelace et al., 2004; Fig. 1). Two >60 m thick sand units called the upper and lower Chicot aquifers comprise the primary aquifer units to the east. In the western part of the study area these units grade into a series of thinner sand units interbedded by impermeable zones of clay and silt (Nyman et al., 1990). In the western region the subunits are informally referred to as the 200ft (61 m), 500ft (152 m), and 700ft (213 m) sand units based on their approximate depths below ground surface (bgs). The sand units of the Chicot aquifer subcrop beneath soils to the north of the study region and dip steeply beneath semipermeable clays and silts to the south and southeast (Fig. 1). The clay/silt units that cap the aquifer sands range from 12 m to over 60 m in thickness (Sargent, 2004). Hence, the Chicot behaves as an unconfined aquifer system where it subcrops to the north and a confined aquifer system to the south. The Chicot aquifer study area is bounded on the west by the Sabine River and to the east by the Atchafalaya River and its alluvial floodplain (Fig. 1). The geologic extent of the Chicot aquifer extends westward, well outside of the hydrologic zone that defines the aquifer system in southwestern Louisiana, and is an important aquifer for the city of Houston, Texas. Recharge to the Chicot aquifer in Louisiana is thought to be limited to rainfall in the north, upward movement from underlying aquifers, and downward infiltration associated with the Atchafalaya boundary river to the east (e.g., Nyman et al., 1990; Sargent, 2004).

Demand for water from the Chicot aquifer is dominated (~70%) by agricultural users, primarily for the irrigation of rice (LDNR, 2012; Sargent, 2011). The cities of Lake Charles and Lafayette are the largest public supply users of groundwater in the region (Fig. 1). Prior to the development of the aquifer in the early 1900s, water flowed from north to south and had a high enough pressure head that wells near the coast were artesian (Nyman et al., 1990). Nyman et al. (1990) estimates that the Chicot aquifer has lost about 0.3 m of potentiometric surface per year since 1900. Currently, the drawdown of the potentiometric surface from pumping due to rice irrigation and industrial needs, largely in Jefferson Davis, Acadia, and Calcasieu Parishes (Fig. 1), has caused groundwater to flow from all directions toward these agricultural and industrial centers. Recent estimates of the water supply gap suggest that the Chicot aquifer is being over-drafted by about 1,320,000 m^3 per day and projections suggest that over-drafts will increase by an additional 460,000 m^3 per day by 2030 (LDNR, 2012).

Previous geochemical investigations of groundwater in the Chicot aquifer have primarily been limited to "snapshots" of the quality of water collected during investigations of domestic wells (e.g., Prakken, 2003; Tollett et al., 2003). These investigations have shown that water in the Chicot is generally of high quality with few contaminants of concern. For example, in a study of 173 domestic wells, Prakken (2003) found that sulfate, fluoride, and nitrate concentrations for all the sampled wells were below US EPA drinking water standards. Tollett et al. (2003) analyzed about 30 wells within the present study area and also found that nutrients (e.g., ammonia, nitrate, and phosphorous) did not exceed US EPA drinking water standards. Some areas of elevated iron, manganese, and chloride concentrations were, however, identified in both investigations. Other studies have reported solely on chloride and/or specific conductivity measurements, demonstrating that

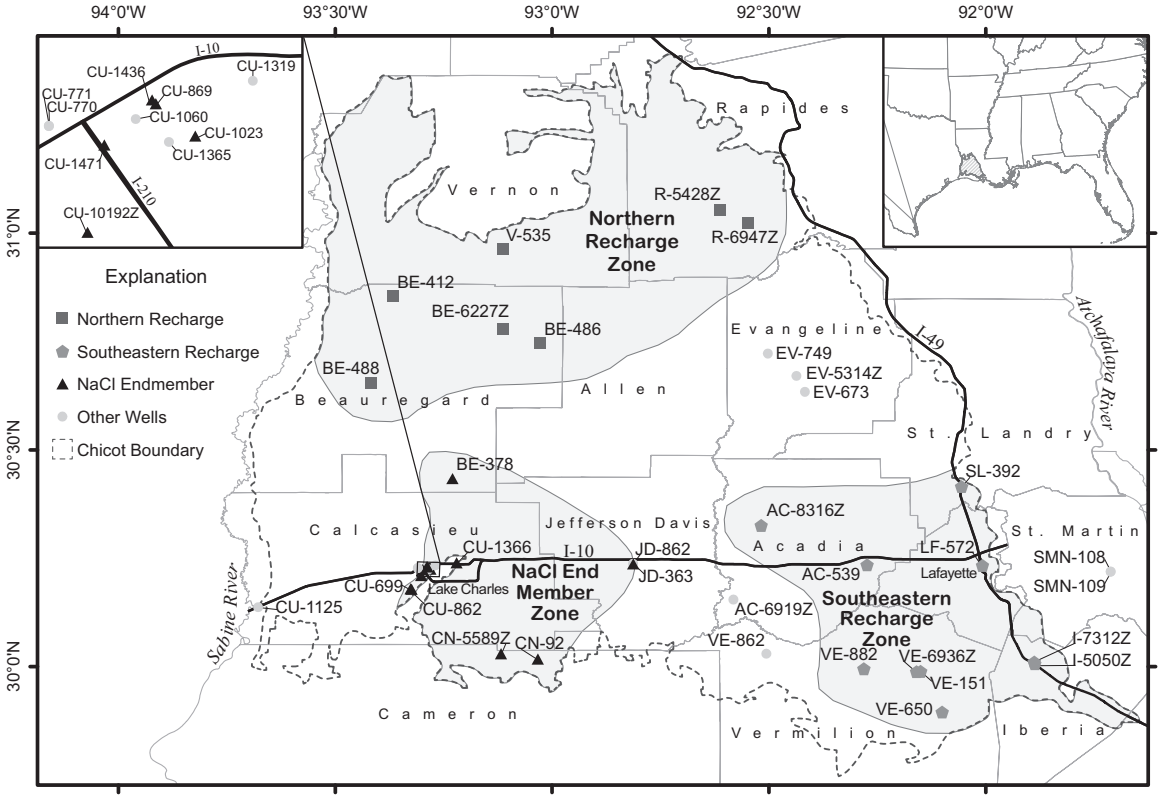

Fig. 1. Location map showing the Chicot aquifer study area and the locations of sampled wells. The shaded regions represent the zones identified in the text that exhibit different groundwater chemistries.

Table 1
Well depths and sample collection information.

Well Name	Location code[1]	Depth (m bgs)	2014	2011	2008	2005	2002	1999	1996	1994	1993
AC-539	2	76.5	■	■	■	■	■	■	■		
AC-6919Z		unknown				■	■	■	■		
AC-8316Z	2	50.3	■	■						■	
BE-378	3	52.4	■	■	■	■	■	■	■	■	
BE-412	1	61.6	■	■	■	■	■	■	■		
BE-486	1	45.7				■	■	■	■		
BE-488	1	79.9	■	■	■	■	■	■	■		
BE-6227Z	1	27.4			■						
CN-5589Z	3	42.7			■	■	■				
CN-92	3	135.0	■	■	■			■	■		■
CU-1023	3	213.7					■	■	■	■	
CU-1060		61.0					■	■	■	■	
CU-10192Z	3	70.1	■	■	■	■					
CU-1125		173.7	■	■	■	■	■	■	■		
CU-1319		155.4								■	
CU-1365		61.9								■	
CU-1366	3	208.8	■	■	■	■					
CU-1436	3	161.5				■	■				
CU-699	3	161.5					■		■	■	
CU-771		73.5					■		■		■
CU-1471	3	160.0	■	■	■						
CU-770		149.4		■	■	■		■			
CU-869	3	160.3						■	■	■	
CU-862	3	170.7	■	■	■	■					
EV-5314Z		54.9						■	■		
EV-749		43.9									■
EV-673		75.3	■	■	■	■	■				
I-5050Z	2	57.3				■	■	■	■		■
I-7312Z	2	54.9	■	■	■						
JD-862	3	212.4	■	■	■	■	■				
JD-363		72.2						■	■		■
LF-572	2	173.7	■	■	■	■	■	■	■	■	
R-5428Z	1	25.9			■	■	■	■	■		
R-6947Z	1	33.5	■	■							
SL-392	2	38.4		■	■	■	■	■	■		■
SMN-108		153.9									■
SMN-109		114.3	■	■	■	■	■	■	■		■
V-535	1	20.1	■	■	■	■	■	■	■		■
VE-650	2	62.5				■	■	■	■		■
VE-6936Z		38.1					■	■	■		
VE-151	2	76.2	■	■	■						
VE-862		75.9	■	■	■	■	■	■	■		■
VE-882	2	85.0	■		■	■	■	■	■		

Gray shaded blocks represent wells and years in which data were collected. [1]Northern recharge zone; [2]Southeastern recharge zone; [3]NaCl endmember zone.

salt water intrusion from the Gulf of Mexico limits the southern extent of freshwater in the Chicot aquifer (Lovelace, 1999; Lovelace et al., 2004). Moreover, this freshwater/saltwater boundary is located progressively northward within the deeper sand unit (s) of the Chicot and Evangeline aquifer systems. In addition to the influence of saltwater in coastal zones, Lovelace et al. (2004) documented areas of high specific conductivity along the border of Jefferson Davis and Calcasieu Parishes and in northwest and central St. Landry Parish (Fig. 1).

3. Methods

3.1. Field parameters and major element chemical data

As part of the Louisiana Department of Environmental Quality's (LDEQ's) Aquifer Sampling and Assessment (ASSET) program, groundwater samples have been collected on a 3-year rotating basis from 14 aquifers in the state of Louisiana. The program began in 1998 and is currently underway (in 2015). Approximately 20 wells within the Chicot aquifer were sampled as part of this program in 2002, 2005, 2008, 2011, and 2014. The exact wells sampled changed slightly from year to year based on availability. Sampling is completed in early spring, typically March through May. Summary reports, which include information on the well locations and chemical data, are completed after each 3-year rotation (LDEQ, 1999, 2003, 2006, 2009, 2012). A smaller subset of wells within the Chicot aquifer was also sampled prior to the creation of the ASSET program in 1993, 1994, and 1996, although fewer chemical parameters were measured. Table 1 lists the wells that were sampled within the Chicot aquifer, the year(s) the wells were sampled, and the depth of each well.

Groundwater samples were collected by using either a submersible field pump, or when available, a dedicated pump that was already installed in the well. For non-continuously operated wells, three well volumes were purged prior to sample collection. There was no need to purge prior to sample collection for continuously operated wells. For wells screened at a depth less than 30 m bgs, a micro-purge process was used. This process purges a small volume of groundwater at a low rate directly from the screened interval to prevent water level drawdown. During this process, field measurements were made for pH, temperature, specific conductance, and salinity using a YSI 600XL™ multi-parameter field instrument that was calibrated prior to each sampling episode. The stabilization of these parameters during micro-purging established that fresh groundwater was being removed from the well.

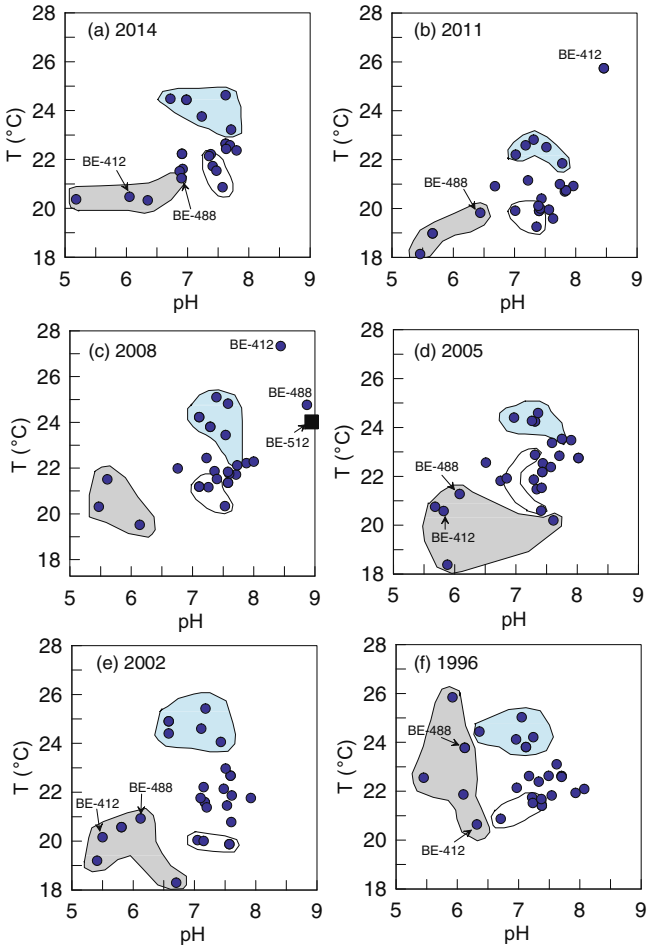

Fig. 2. Temperature plotted as a function of pH for sampled groundwater wells in 2014 (a), 2011 (b), 2008 (c), 2005 (d), 2002 (e), and 1996 (f). Wells associated with the northern recharge zone, southern recharge zone, and NaCl endmember zone are shaded gray, unshaded, and shaded blue, respectively. Temperature and pH data for 1999 are available, but were not shown to conserve space. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

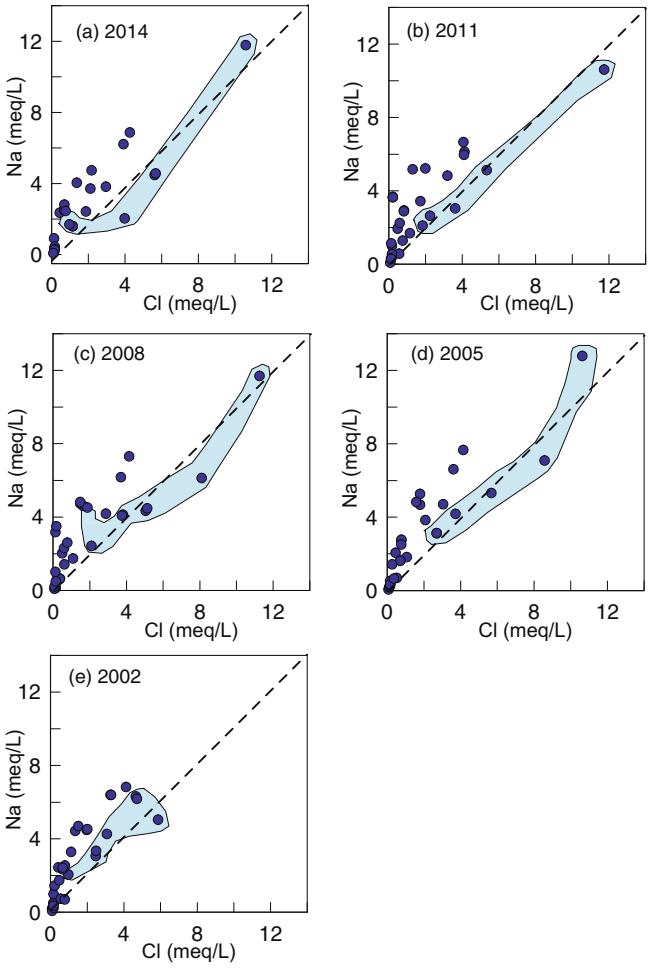

Fig. 3. Na (meq/L) versus chloride (meq/L) for sampled groundwater wells in 2014 (a), 2011 (b), 2008 (c), 2005 (d), and 2002 (e). Wells associated with the NaCl endmember zone are shaded blue. Na data were not available prior to 2002. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Field measurements were recorded for each well, including the wells where the micro-purge process was not used.

Unfiltered water was collected for measurements of alkalinity, major elements, and trace elements in 500 mL plastic sample bottles. Additional samples were collected in separate containers for analysis of trace elements, nutrients, volatile organic compounds, semi-volatile organic compounds, pesticides, and PCBs (these parameters are not discussed in this study). Field blanks and duplicate samples prepared in the field by ASSET personnel and matrix-spiked samples prepared by the analyzing lab were used for quality control. Concentrations of the measured parameters were below detection or present at background levels in the field blanks. Concentrations of elements in duplicate samples matched, within analytical uncertainties, the concentrations of the same elements in the primary samples collected from the same well. Recovery from matrix spike samples met EPA operating guidelines for the given methods.

Sample containers used by the ASSET program were supplied by the analyzing laboratory. Containers were delivered pre-cleaned. In cases where samples required acidification the proper quantity and type of acid was pre-added to each container by the analyzing laboratory. Preprinted labels were affixed to each container identifying sample number, sample date, analyte group, and preservative. Sample collection time was recorded on the label and the label secured to the container with clear packing tape. EPA standard methods SM2320B and 300.0 were used for measuring the concentrations of alkalinity and Cl, respectively. EPA method 200.8 was used to measure the concentrations of Ca, Mg, and Na. These are the only laboratory parameters included in this study. Once filled, sample containers were placed in an ice chest to attain and maintain a temperature $\leqslant 4$ °C. To ensure holding times were not exceeded, samples were transported by ASSET personnel to the analyzing laboratory. Normal chain-of-custody procedures were followed requiring signed acceptance by the analyzing lab.

Over the >20 years that samples have been collected by LDEQ personnel, several analytical laboratories have been utilized. The vast majority of the analyses were performed by three laboratories; (1) LDEQ's in-house analytical laboratory in Baton Rouge Louisiana, (2) Pace Analytical in St. Rose, Louisiana, and (3) Accutest (formerly Southern Petroleum Labs) in Lafayette, Louisiana. Other labs used to a lesser degree were Gulf Coast Analytical Laboratory Environmental Testing and Consulting, and American Analytical Testing Service.

3.2. Oxygen and hydrogen isotope data

During the 2014 ASSET sampling period, 60 mL glass vials with sealing lids (to prevent evaporation) were additionally filled for analysis of O and H isotope data. These samples were sent to the

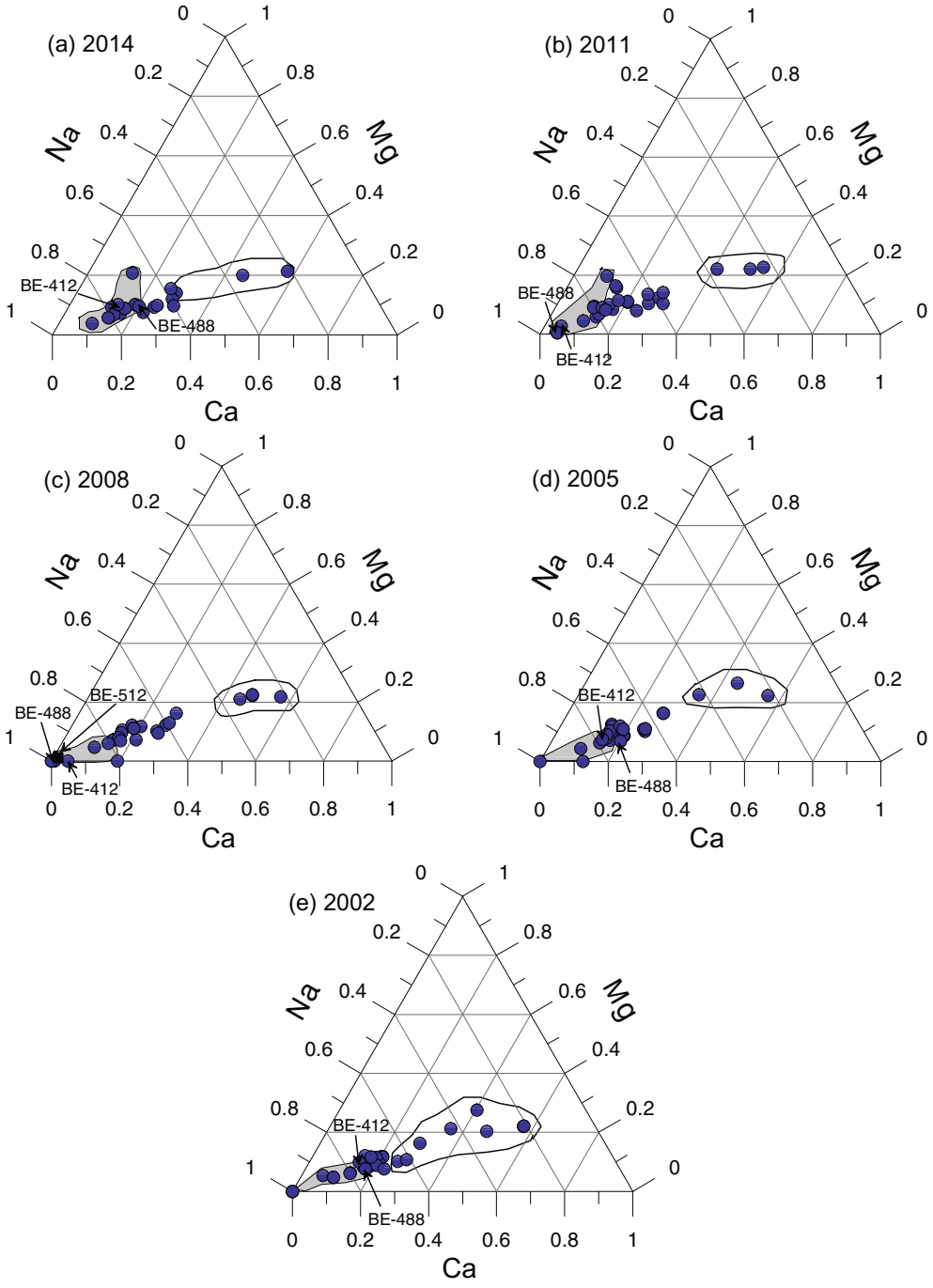

Fig. 4. Ternary plot of the relative proportions of Na, Ca, and Mg (all in meq/L) for sampled groundwater wells in 2014 (a), 2011 (b), 2008 (c), 2005 (d), and 2002 (e). Wells associated with the northern recharge zone are shaded gray and wells associated with the southern recharge zone are unshaded. Data were not available prior to 2002.

Center for Trace Analysis at the University of Southern Mississippi for analysis using a Picarro™ laser analysis system. Results are reported relative to Vienna Standard Mean Ocean Water. Average 2σ uncertainties based on replicate analysis for $\delta^{18}O$ and $\delta^{2}H$ were 0.08‰ and 0.46‰, respectively.

4. Results and discussion

4.1. pH and temperature

Temperature and pH data for all the sampled wells in the Chicot aquifer for 2014, 2011, 2008, 2005, 2002, and 1996 are presented in Fig. 2. In many years, the pH and temperature data alone appear to be sufficient to identify the recharge areas within the Chicot aquifer. The northern recharge zone in the Chicot (the gray shaded region in Fig. 2) is characterized by low pH and low temperature. Because rainwater is in equilibrium with atmospheric carbon dioxide and is unbuffered by other chemical constituents, its natural pH is around 5.5 (Drever, 1988). The lower temperature of the groundwater in the northern recharge area likely reflects the shallowness of the aquifer that crops out in this region (Table 1). Moreover, since the temperature of rain during the early spring sampling periods is lower than that for average groundwater, the temperature of groundwater could be further influenced by recharge. Some of the groundwater temperatures recorded in the 1996 sampling

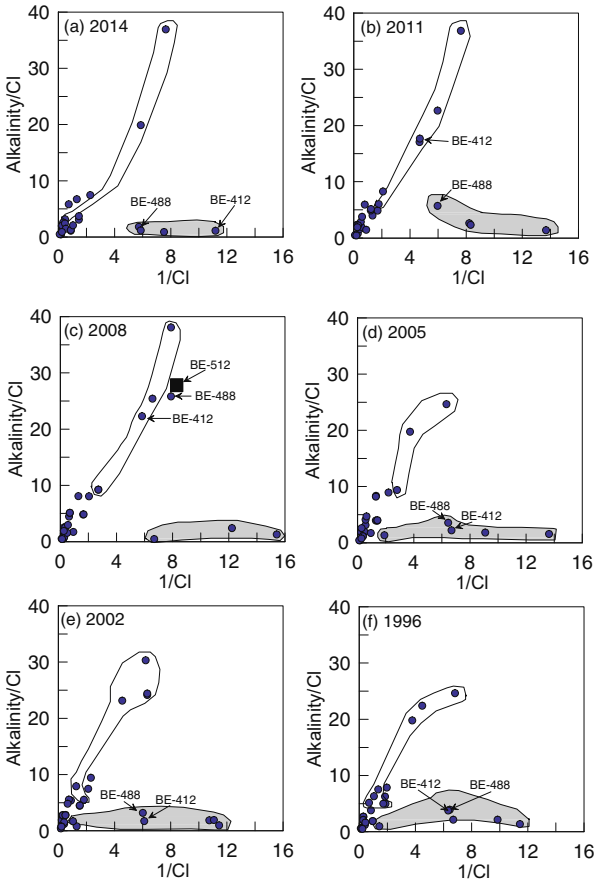

Fig. 5. Alkalinity/Cl versus 1/Cl for sampled groundwater wells in 2014 (a), 2011 (b), 2008 (c), 2005 (d), 2002 (e), and 1996 (f). Concentrations in meq/L were used for calculating ratios. Wells associated with the northern and southern recharge zones are shaded gray and are left unshaded, respectively. Alkalinity and chloride data for 1999 are available, but were not shown to conserve space.

event support the latter explanation in that there was a shift in groundwater temperatures to higher values (Fig. 2) that corresponded with a change in the sampling time period from early spring (for all other years) to late summer for the 1996 samples. Note that in 2008 (Fig. 2c) and 2011 (Fig. 2b) samples from BE-488 and/or BE-412 varied substantially from the temperature and pH profiles of the other wells in the northern recharge zone. This shift to higher temperature and higher pH water probably represents a contribution from a deeper aquifer source (see additional discussion in Section 5.1). The northern recharge zone is additionally characterized by low salinity water. The average salinity of the water in all the wells sampled within the northern recharge area was 0.02, 0.03, 0.02, 0.03, 0.03, and 0.03 parts per thousand (ppt) for sample years 2014, 2011, 2008, 2005, 2002, and 1996, respectively (data not shown).

A second zone of recharge in the southeastern part of the Chicot aquifer system is characterized by its lower temperatures but circumneutral pH (The unshaded region in Fig. 2). The higher pH of these samples relative to the northern recharge zone likely reflects the fact that the recharge is not as directly influenced by rainwater. As suggested previously by Nyman et al. (1990) and Lovelace et al. (2004), recharge in the southeast part of the Chicot aquifer is most likely occurring through connections to the alluvial fill aquifers associated with the Vermilion and/or Atchafalaya Rivers (Fig. 1). The somewhat shallower wells with connectivity to surface waters would account for the lower temperatures (Table 1), while the higher pH is probably attributable to buffering through water–rock interactions in the associated shallow aquifer systems. The average

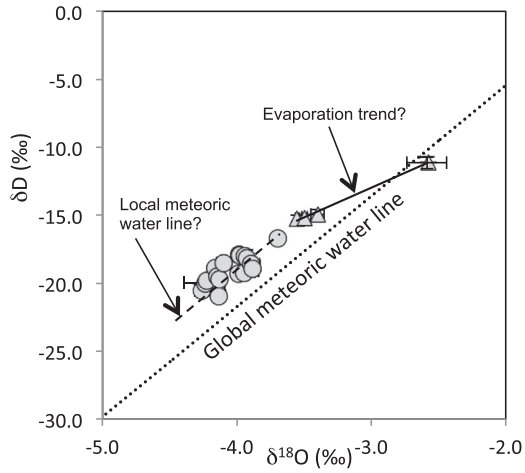

Fig. 6. Plot of δD versus $\delta^{18}O$ for groundwater samples collected in 2014. The dotted line represents the global meteoric water line while the smaller dashed line represents the approximate location for a hypothesized local meteoric water line associated with the samples outside the southeastern recharge zone (open circles). The solid line best fits the data from wells that fall within the southeastern recharge zone (open triangles). Error bars represent 2σ uncertainties. Error bars smaller than the size of the symbols are not shown.

salinity of the groundwater in this region was 0.30, 0.25, 0.27, 0.28, 0.26, 0.26, and 0.24 ppt for sample years 2014, 2011, 2008, 2005, 2002, and 1996, respectively (data not shown).

Finally, a third group of water samples consistently stood out as a cluster because of their elevated temperature relative to the other samples (the blue shaded zone in Fig. 2). Most of these samples are additionally characterized by high salinity values. The average salinity of this group of samples was 0.35, 0.38, 0.40, 0.42, 0.32, 0.43, and 0.36 for sample years 2014, 2011, 2008, 2005, 2002, and 1996, respectively (data not shown). The spatial extent of the wells that were identified as part of the high temperature and salinity zone is limited to a zone in the south and southwest part of the Chicot aquifer (Fig. 1). Of the twelve wells that have exhibited these elevated temperatures, nine of them are over 120 m deep (Table 1). It is possible that the three shallower wells (<120 m bgs) are influenced by waters in the deeper sand units that have ascended into the shallower sand units during pumping.

4.2. Major element chemistry

The northern recharge, southeastern recharge, and higher temperature zone in the southwest that were identified through temperature, pH, and salinity relationships (Fig. 2) can be further delineated through examination of major element chemistry. The chemistry of the Chicot aquifer is dominated by sodium–calcium–magnesium–bicarbonate–chloride (Na–Ca–Mg–HCO_3–Cl) waters. Very little potassium or sulfate are present relative to the other ions. Fig. 3 illustrates the relationship between the concentrations of Na and Cl in the samples collected from the Chicot aquifer in 2014 (a), 2011 (b), 2008 (c), 2005 (d), and 2002 (e). Sodium was not measured in sampling events prior to 2002. The 1:1 Na versus Cl dashed line is indicative of waters influenced by the dissolution of a pure NaCl endmember. Water in the northern recharge zone is characterized by a low salinity Na–Cl composition that is indicative of rainwater. Rainwater chemistry is similar to that of diluted seawater, which has a Na versus Cl ratio of a bit less than one (Drever, 1988). Excepting the low-salinity northern recharge samples, the higher-salinity, higher-temperature waters (identified in Fig. 2) generally fall closest to the 1:1 Na versus Cl trend line (blue shaded zone in Fig. 3), suggesting that this water is influenced by seawater (Na/Cl ~ 0.8) or a brine formed from

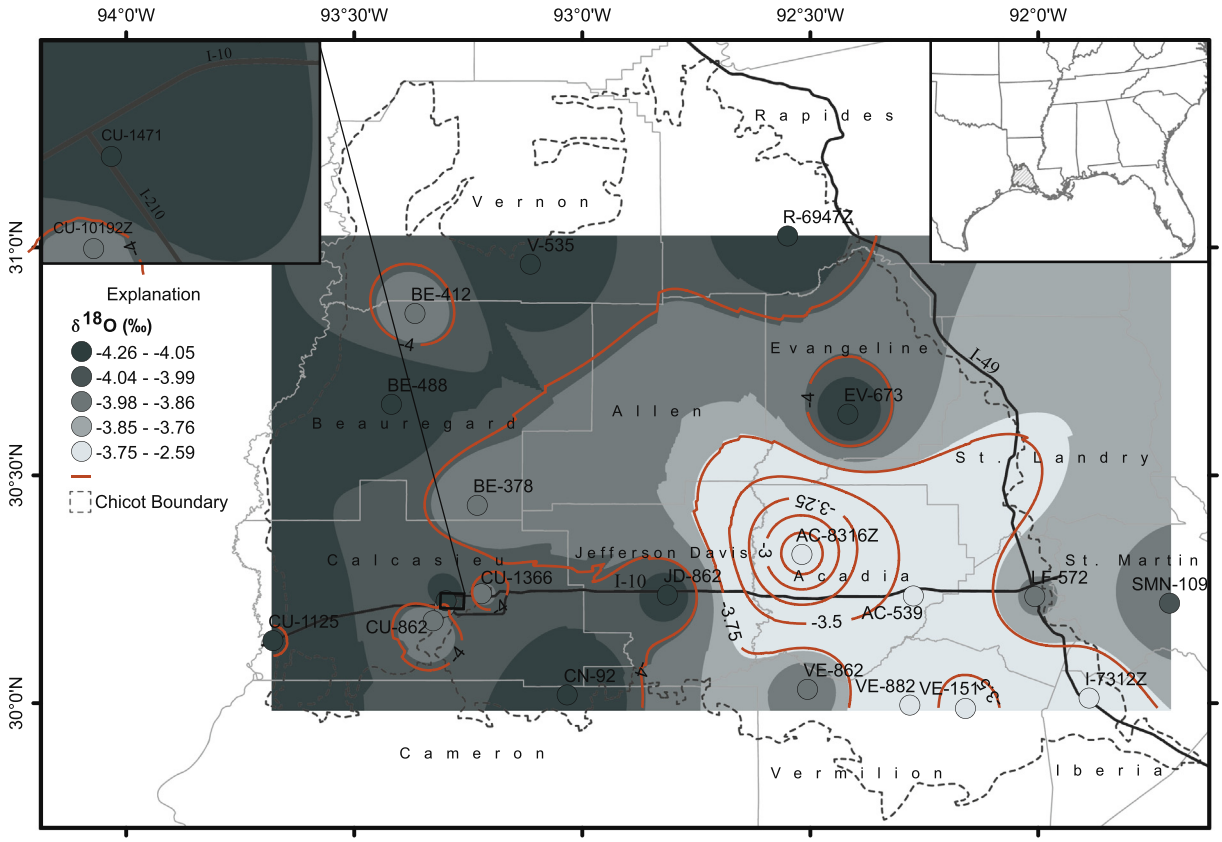

Fig. 7. Contour map of $\delta^{18}O$ values measured for groundwater samples collected in 2014. Contours were created in ArcGIS using inverse distance weighted interpolation based on the point values associated with each monitoring well. Groundwater in the southeastern recharge zone corresponds with the highest $\delta^{18}O$ values.

the dissolution of evaporative salt (Na/Cl ~ 1.0). Hence, we refer to the region where this groundwater chemistry is present as the "NaCl Endmember region" (Fig. 1). The chemistries of most all the remaining samples fall above the 1:1 NaCl line, indicating the presence of Na–HCO_3 waters (the excess Na cations must be balanced by bicarbonate anions). Sodium bicarbonate waters often develop through interactions with siliciclastic rocks where the Ca and Mg in Ca–Mg–HCO_3–waters substitute for Na in clay minerals (e.g., Foster, 1950; Hanor, 1982).

Fig. 4 is a ternary plot illustrating the relative distributions of the concentrations for the three major cations, Na, Ca, and Mg (in milliequivalents/L) in the groundwater collected from the Chicot aquifer in 2014 (a), 2011 (b), 2008 (c), 2005 (d), and 2002 (e). The southeastern recharge zone is characterized by Ca and Mg-rich waters (outlined area with no fill in Fig. 4). The northern recharge zone is dominated by more Na-rich waters with minor amounts of Ca and Mg (gray shaded area in Fig. 4). In 2011 (Fig. 4b) and 2008 (Fig. 4c), samples from BE-412 and BE-488 shift to an even richer Na composition. There appears to be a trend in the evolution of the Ca–Mg chemistry of the southeastern recharge zone toward a more Na-rich composition in the other parts of the aquifer. This trend could be indicative of mixing of two distinct water chemistries, and/or it may reflect water–rock interaction leading to a more Na-rich waters. As described above, the Na–HCO_3 waters in the Chicot aquifer may be produced from the substitution of Na in clay minerals for Ca or Mg in Ca–Mg–HCO_3 waters.

Fig. 5 illustrates the relationship of the meq/L of alkalinity relative to chloride as a function of the inverse chloride concentration for years 2014 (a), 2011 (b), 2008 (c), 2005 (d), 2002 (e), and 1996 (f). The alkalinity/Cl ratio of water in the southeastern recharge zone (outlined area without fill in Fig. 5) steadily decreases as a function of increasing Cl concentration, suggesting that the more alkaline waters of the southeastern recharge zone are mixing with the more Cl-rich waters of the south and central parts of the Chicot aquifer. The northern recharge zone (gray shaded area in Fig. 5) is characterized by low Cl concentrations and low alkalinity/Cl ratios (less than ~5) relative to the other samples. The groundwater of the northern recharge zone becomes more Cl-rich as it evolves, but the alkalinity/Cl ratio does not appreciably change. This indicates that there is no direct mixing of waters from the two recharge zones. Water from the northern recharge zone evolves (via water rock interactions) as it travels southward and mixing occurs between some of these more evolved waters and the southeastern recharge zone.

Samples collected from BE-412 in 2011 (Fig. 5b) and 2008 (Fig. 5c) and the sample from BE-488 in 2008 (and perhaps in 2011; Fig. 5c) deviate substantially from the chemistry of the northern recharge zone. During these years BE-412 and BE-488 had an elevated alkalinity/Cl ratio (Fig. 5) in addition to a higher pH and temperature (Fig. 2b and c). The groundwater in BE-412 and BE-488 at these times is characterized by a Na–HCO_3 composition, which is similar to that of the underlying Evangeline aquifer (see additional discussion in Section 5.1).

4.3. Oxygen and hydrogen isotopes

Oxygen and H isotope data collected from the 2014 sampling event are plotted in Fig. 6 and are compiled in Table S-1. The global meteoric water line, which reflects the relationship between O and H isotopes in average global rainfall, is illustrated in Fig. 6 for reference. Oxygen isotopes in the groundwater from the Chicot aquifer varied over a modest range from −4.26‰ to −2.59‰. The spatial distribution of $\delta^{18}O$, illustrated in Fig. 7, shows that the

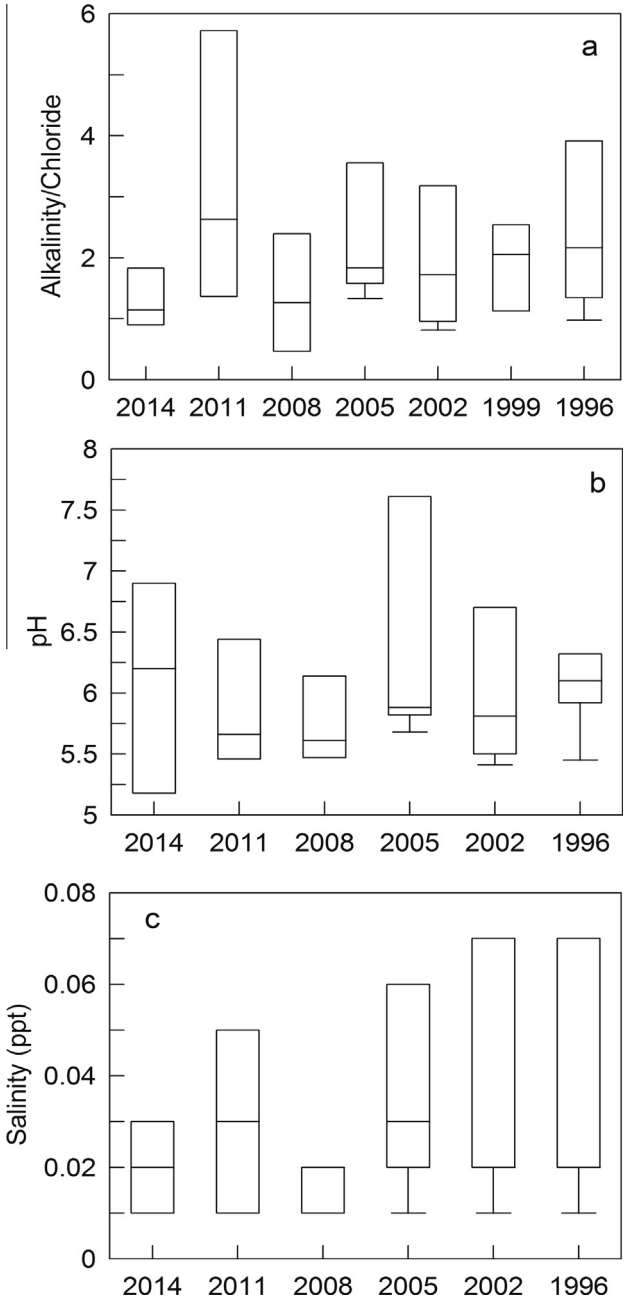

Fig. 8. Box whisker plot illustrating the statistical variations of the alkalinity/Cl ratio (a), pH (b), and salinity (c) for samples collected within the northern recharge zone for the years when at least 4 or more samples were collected. For years 2014, 2011, 2008, 2005, 2002, 1999, and 1996, $n = 4$, 3, 3, 5, 5, 4, and 5, respectively. Several of these samples were not measured for pH or salinity in 1999 and are therefore this year was not included for these measures. In some instances the maximum and minimum values (i.e., whiskers) are the same as the quartile limits.

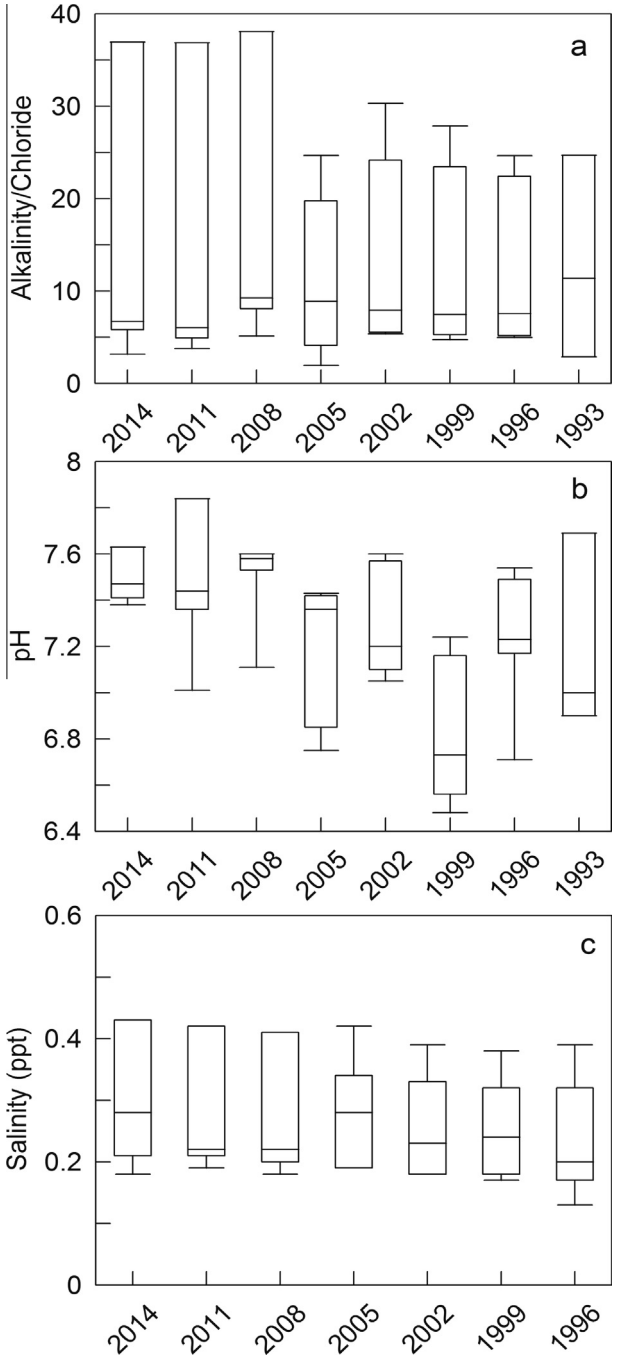

Fig. 9. Box whisker plot illustrating the statistical variations of the alkalinity/Cl ratio (a), pH (b), and salinity (c) for samples collected within the southeastern recharge zone for the years when at least 4 or more samples were collected. For years 2014, 2011, 2008, 2005, 2002, 1999, 1996, and 1993, $n = 5$, 5, 5, 6, 7, 7, 7, and 4, respectively. In some instances the maximum and minimum values (i.e., whiskers) are the same as the quartile limits.

heaviest values are associated with the southeastern recharge zone.

The water isotopes of groundwater samples directly reflect those of the precipitation that recharged the groundwater (Kendall and McDonnell, 1998). Hence, it is clear that the southeastern zone of recharge is unique relative to the northern recharge zone and other areas of the Chicot aquifer in that precipitation of a different temperature or that underwent more evapotranspiration recharged the groundwater in this area. Because the fractionation factor for rain formation from a cloud is temperature dependent, O and H isotopes in rain are closely linked to temperature and therefore latitude. Warmer precipitation is isotopically heavier than cooler precipitation (e.g., Faure, 1977). Moreover, O and H isotopes in water bodies evolve to become isotopically heavier during evaporation because the lighter isotopes preferentially enter the vapor phase. Kinetic differences in the fractionation of O versus H isotopes due to humidity and salinity lower the slope of the meteoric water line during evapotranspiration (Kendall and McDonnell, 1998). Other factors that might influence O and H isotopes like the "rainout effect", which refers to the continual isotopic evolution of rainwater related to the amount of rain that

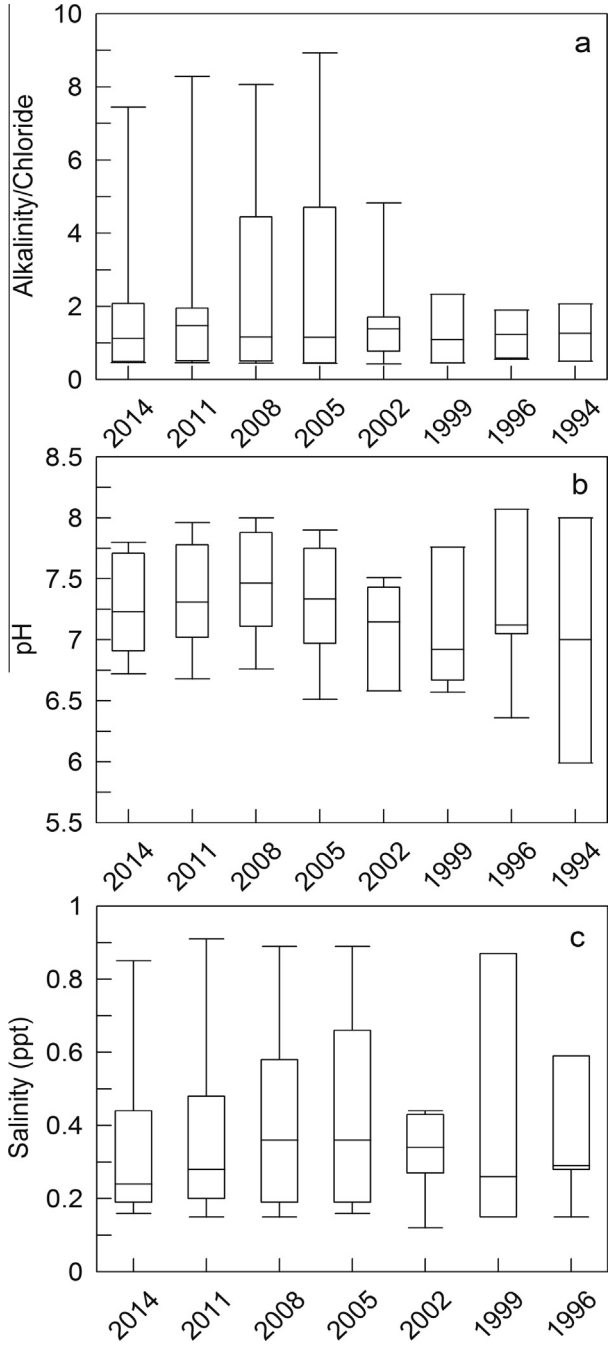

Fig. 10. Box whisker plot illustrating the statistical variations of the alkalinity/Cl ratio (a), pH (b), and salinity (c) for samples collected within the NaCl endmember zone for the years when at least 4 or more samples were collected. For years 2014, 2011, 2008, 2005, 2002, 1999, 1996, and 1994, $n = 7, 7, 8, 7, 6, 4, 5$, and 4, respectively. In some instances the maximum and minimum values (i.e., whiskers) are the same as the quartile limits.

falls are unlikely to be meaningful over the regional scale of this investigation.

The O and H isotope data in our study seem to best-fit the evapotranspiration scenario (Fig. 6). Although the data are too limited to construct a robust local meteoric water line, we can estimate such a line with the same slope as the global meteoric water line that cuts through the data (Fig. 6). The addition of a separate best-fit line only for the data collected from wells in the southeastern recharge zone demonstrates a substantial break in slope from the possible meteoric water line. This shift is suggestive of an evaporation trend (Fig. 6). The suggestion of an evaporative influence on groundwater recharge in this area fits well with the idea that recharge is coming from the shallow alluvial aquifers associated with rivers and swamps as opposed to directly from rainfall. Groundwater recharged from standing water bodies often has an evaporative component that can be identified using O and H isotopes (e.g., Dinçer et al., 1979).

5. Changes in water chemistry over time

Box and whisker plots are used to summarize the alkalinity/chloride ratios, pH, and salinity for all the samples in the northern recharge zone, southeastern recharge zone, and the NaCl endmember zone in Figs. 8–10, respectively. Data are summarized for every sampling year where at least 3 data points were available within the respective zone. Box and whisker plots treat the data statistically, illustrating the median value, first quartile, third quartile, and max and min sample values for each sampling period.

5.1. Northern recharge zone

For this assessment, samples from BE-412 and BE-488 from 2008, from BE-412 from 2011, and from BE-488 in 1999 were excluded, as their chemistries were most likely influenced by the underlying Evangeline aquifer system during these sampling events (see discussion below). The chemistries of the remaining wells have been relatively consistent over the last ~18 years. For example, the alkalinity/Cl ratio of the samples in the northern recharge zone ranged from a low of 1.14 in 2014 to a high of 2.63 in 2011 (Fig. 8a). The median pH of wells in the northern recharge zone varied over a narrow range from 5.61 in 2008 to 6.20 in 2014 (Fig. 8b). The median values for salinity were similarly consistent, ranging from 0.02 to 0.03 ppt (Fig. 8c). The interquartile distributions for salinity, however, were greater in 1996, 2002, and 2005, indicating more variability and some higher individual salinity values than were present in 2008, 2011, and 2014.

Groundwater samples from BE-412 and BE-488 sometimes exhibited chemistries with higher temperature, higher alkalinity, and higher pH than the other samples in the northern recharge zone. This indicates that water from outside the northern recharge zone was being captured by pumping of the Chicot aquifer in these years (in 2011, 2008, and 1999) at these well locations. For comparison purposes, we have plotted the chemical data for well BE-512 (measured in 2007), which is located within 50 m of BE-488, in Figs. 2c, 4c, and 5c. Well BE-512 is 280 m deep and is screened in the Evangeline aquifer, while BE-488 is 80 m deep and is screened in the Chicot aquifer. It is apparent that the pH, temperature, and alkalinity/chloride ratio of the Evangeline aquifer, as measured in 2007 from BE-512, is almost identical to that measured for well BE-488 in 2008 (Figs. 2c, 4c, and 5c). Pumping at a rate that is greater than can be supported by the Chicot in this region likely resulted in the capture of Na–HCO_3-rich waters from the underlying Evangeline aquifer. This suggests that the northern recharge zone of the Chicot aquifer is susceptible to over-pumping and that the Chicot and Evangeline aquifers are hydraulically connected in the area along the northwestern margin of the study area (Fig. 1). This is important because the water chemistry of the Evangeline aquifer, although of reasonable quality in this area, is substantially more Na- and HCO_3-rich than that of the Chicot. This could affect some agricultural and industrial users, who are not expecting water of such a different character. Moreover, there is an increased risk of saltwater intrusion through pumping of the Chicot aquifer at levels that could promote the northward

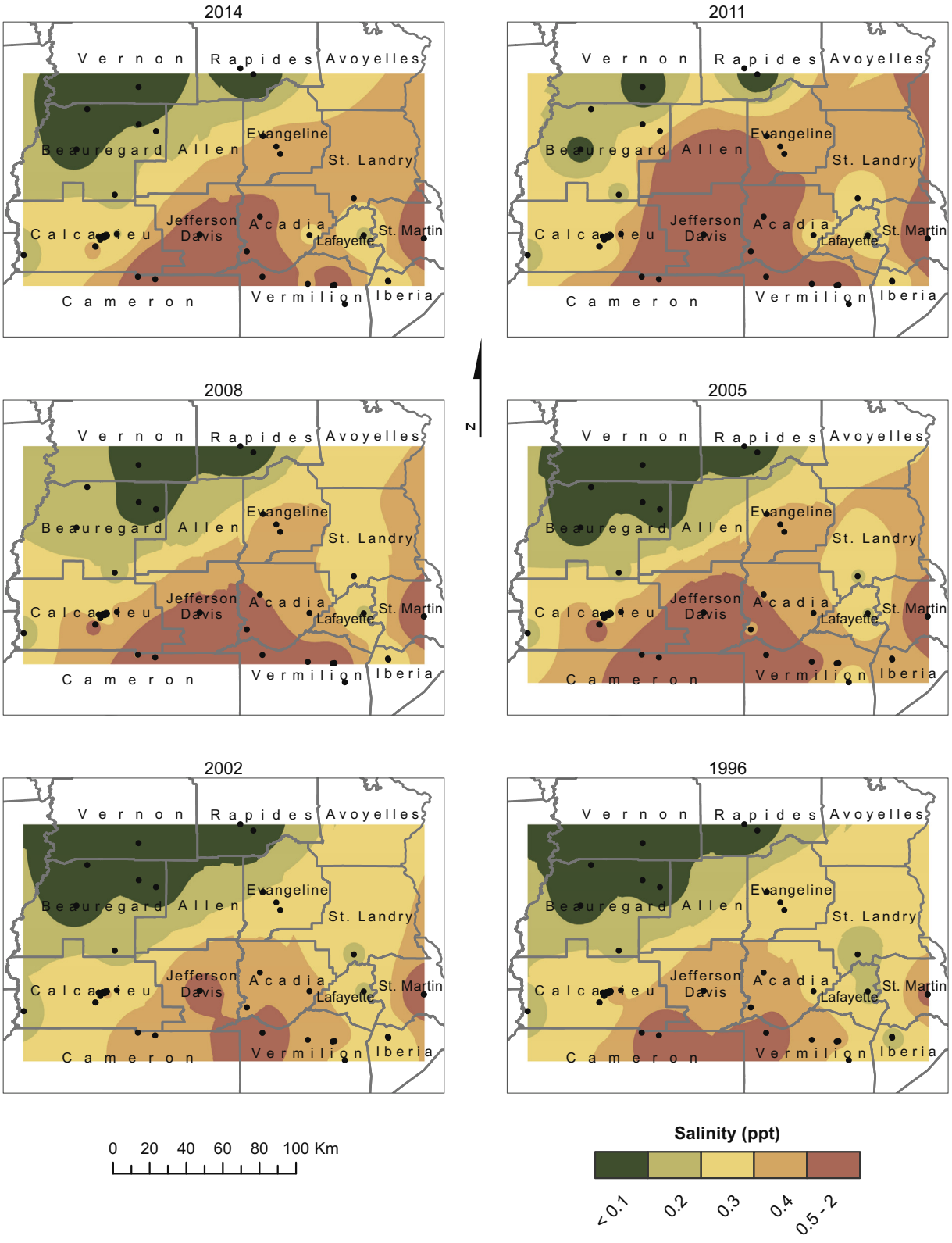

Fig. 11. Contour map of salinity values measured for groundwater samples collected in 2014, 2011, 2008, 2005, 2002, and 1996. Salinity measurements were also available for 1999 but were not shown to conserve space. A more limited set of salinity data were available for 1993 but these were not sufficient for contouring the entire study region. Contours were created in ArcGIS using inverse distance weighted interpolation based on the point values associated with each monitoring well.

migration of salt water within the Evangeline aquifer. The freshwater/saltwater boundary in the deeper Evangeline aquifer system lies much further northward than the same boundary within the shallower Chicot aquifer (Nyman, 1989).

5.2. Southeastern recharge zone

The median values of the alkalinity/Cl ratio in the southeastern recharge zone varied from a minimum of 6.0 in 2011 to a

maximum of 11.4 in 1993 (Fig. 9a). The interquartile range and maximum values increase dramatically in 2008, 2011, and 2014, which corresponds with the sampling of well I-7312Z, which has an alkalinity/Cl ratio of ~37. This well had not been sampled prior to 2008. The groundwater in I-7312Z is likely the most representative of the end member chemistry of the groundwater in the southeastern recharge zone. The median pH of water in the southeastern recharge zone varied from 6.73 to 7.35 during the period from 1993 to 2005, but increased to 7.47, 7.44, and 7.58 in 2014, 2011, and 2008, respectively (Fig. 9b). This increase in pH is related to the increased alkalinity in several samples, including those from well I-7312Z, described above (Fig. 9a). Finally, the median salinity of water in the southeastern recharge zone ranged from 0.2 ppt in 1996 to 0.28 ppt in 2005 and 2014 (Fig. 9c). The interquartile ranges expanded measurably in 2008, 2011, and 2014, indicating the presence of more samples of slightly higher salinity than in previous years. However, given the low sample numbers collected it is not possible to establish a clear trend.

5.3. NaCl endmember zone

The NaCl endmember zone, which is associated with higher salinities and temperatures relative to other samples, has maintained a remarkably consistent median alkalinity/chloride ratio over time. For the last 20 years, the median values for alkalinity/Cl have ranged from a low of 1.12 in 2014 to a high of 1.47 in 2011 (Fig. 10a). The median pH of the NaCl endmember zone has also remained consistent for the last 20 years, ranging from a low of 6.92 in 1999 to a high of 7.47 in 2008 (Fig. 10b). The median salinity of this zone ranged from a low of 0.24 ppt in 2014 to a high of 0.36 ppt in 2005 and 2008 (Fig. 10c). The maximum values for salinity in the NaCl endmember zone for all years are attributable to well CN-92, except for the year 2002 when the well was not sampled (Table 1). Well CN-92 is a deep well (135 m bgs) that is close to the coastline and appears to be near the saltwater/freshwater interface in the Chicot aquifer. Despite its location and the potential for increasing levels of saltwater intrusion, the salinity in CN-92 has remained relatively consistent from 1999 to 2014.

5.4. Changes in salinity in the Chicot aquifer

Contour maps of salinity values for all the sampled wells in the Chicot aquifer for 1996, 2002, 2005, 2008, 2011, and 2014 are presented in Fig. 11. The areas with the highest salinity are closer to the coast and likely reflect the influence of salt water intrusion. The extent of the highest salinity zone (0.5–2 ppt) was least in 1996 and 2002, suggesting a modest trend toward increasing salinity over time (Fig. 11). The high salinity zone reached its greatest extent in 2011, which was a severe drought year for the region (e.g., Lal et al., 2012; Tadesse et al., 2015). Guidry and Pruitt (2012) estimated that there was $436 million in damage to crops in Louisiana from the 2011 drought. The northward encroachment of the high salinity zone in 2011 likely reflects increased pumping of wells in the Chicot aquifer in response to the lack of rain and available surface water. The expansion of the high salinity zone in 2011 estimated by the contour map (Fig. 11) also corresponds with a close fit of the samples within the NaCl endmember zone to a 1:1 Na/Cl ratio (Fig. 3b), hinting at increased saltwater encroachment in this region. The fact that median salinity values in the NaCl endmember zone did not increase appreciably in 2011 (Fig. 10c) suggest that some of the most significant changes in increasing salinity were with samples on the periphery of this zone. Fig. 5 is particularly effective in showing an apparent mixing trend between the geochemistry of the southern recharge zone and that of the NaCl endmember zone. The estimated extent of the lowest salinity zone (<0.1 ppt) in the northern recharge area reached a minimum in 2011. This likely reflects the fact that aquifer water stored for a longer period of time (with longer water–rock exposure) was utilized because less rainfall was available for recharge during this severe drought year.

6. Conclusions and sustainability of the Chicot aquifer system

In this study we identified three distinct zones of groundwater geochemistry within the Chicot aquifer system (Fig. 1). The geochemistry of the groundwater within the wells that fall outside of these zones can be produced via mixing of these three endmembers and/or through water–rock interactions that shift the groundwater toward a more Na–HCO_3 composition. In addition to the recharge zones in the north and southeast, we see some evidence of recharge from underlying aquifer units. For example, in years 1999, 2008, and 2011 (either or both) wells BE-412 and BE-488, which are screened in the Chicot aquifer, appear to be tapping water with a geochemistry (temperature, salinity, alkalinity, etc.) matching the underlying Evangeline aquifer. Furthermore, the elevated groundwater temperatures found in several of the shallow wells within the NaCl endmember zone may suggest that deeper, warmer waters are being captured by pumping.

The expansion in the spatial extent of groundwater with elevated salinity during the 2011 drought demonstrates that the Chicot aquifer responds rapidly to perturbations in available recharge and demand. The short-term resiliency of the Chicot aquifer is remarkable in light of the fact that it has been substantially overdrafted for many years and in some areas has probably lost more than 30 m of potentiometric surface. The long-term sustainability of the Chicot aquifer system and exactly how long it can be counted on to maintain this level of resiliency, however, is more uncertain. Increased groundwater pumping in the Chicot aquifer in response to drought and increased demand will accelerate interaction with the underlying saltier aquifer units, ultimately increasing the extent of salt-rich encroachment. Furthermore, if aquifer storage and the hydraulic head continue to drop over time, it will become increasingly difficult for the aquifer system to rebound from severe drought. Isotope and bulk geochemical data indicate that the southeastern zone of recharge plays an important, and possibly an increasingly larger, role in meeting the demand for groundwater in the Chicot aquifer. There may be important long-term implications if large (or expanded) amounts of recharge are tied to the shallow aquifers associated with river systems in the southeastern part of the Chicot aquifer. It is unclear, for example, as to what extent this recharge could influence the base flow level of the connected surface water bodies and the associated riparian vegetation. This investigation demonstrates the importance of collecting geochemical data for evaluating groundwater associated with sensitive coastal aquifer systems over extended periods of time.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2015.12.

022. These data include Google maps of the most important areas described in this article.

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